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Mononuclear bromotellurates (IV) with pyridinium-type cations: Structures and thermal stability

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ABSTRACT

Eleven new bromotellurate complexes cation$_2$[TeBr$_6$]·XH$_2$O (cation = R-PyH$^+$, R = 2-Me (**1**), 3-Me (**2**), 2-I (**3**), 3-Cl (**4**), 3-Br (**5**), 2,6-Me (**6**), 2,4,6-Me (**7**); cation = R-Py$^+$, R = 1-Et (**8**) 1,3-Me (**9**), 1,4-Me (**10**) and 1-Me-3,5-Br-4-(NMe$_2$) (**11**)) were prepared and characterized by X-ray diffractometry. Thermal stability of abovementioned complexes, as well as previously reported (4-MePyH)$_2$[TeBr$_6$] (**12**) and (2-BrPyH)$_2$[TeBr$_6$] (**13**), was studied by thermogravimetric analysis (TGA).

1. Introduction

Although halide complexes of late transition (Cu, Ag) and post-transition metals (Pb, Sb and Bi) are known since many decades, they continue to attract attention due to a number of promising physical properties. The most remarkable features of this class of compounds are: ferroelectricity and ferroelasticity [1–4], thermochromism [5,6] and solvatochromism [7], photocatalytic activity which is especially common for Ag derivatives [8–11] etc. A particularly "hot" application area is photovoltaics: since bromo- and iodometalates can be utilized as light absorbers in solar cells, many efforts are concentrated on search of compounds that may become alternative for methylammonium lead iodide (MAPI), the most commonly studied iodoplumbate [12–16]. Therefore, further research of halide complexes is highly encouraged.

In 2017, we reported [17] four new bromotellurate-polybromide hybrids where [TeBr$_6$]$^{2-}$ anions are connected by Br$_2$ linkers into zigzag or linear chains. Since it is well-known that chemistry of halometalates is generally cation-dependent and the structure of anionic part may vary, we decided to extend the range of cations used in reaction: "TeO$_2$ + HBr + Br$_2$ + cationBr" (in [17], cations were PyH$^+$, 2- and 4-MePyH$^+$ and 1-MePy$^+$), using a set of other pyridinium derivatives. Surprisingly, we found that formation of polybromide/bromotellurate moieties does not occur in many cases. Instead, there form only mononuclear cation$_2$[TeBr$_6$] (in some cases isolated as solvates) which were characterized by XRD. Although there are over 30 structures of the bromotellurates of this sort (see below), to the best of our knowledge systematic studies of thermal stability have not been reported. In order to fill this gap, we conducted TGA for an extended series of the complexes, including (4-MePyH)$_2$[TeBr$_6$] (**12**) and (2-BrPyH)$_2$[TeBr$_6$] (**13**) reported earlier [17,18].

2. Experimental part

2.1. General remarks

All reagents were obtained from commercial sources and used without additional purification. 1-ethylpyridinium bromide, 1,3-methyl, 1–4,methyl and 1-methyl-4-dimethylaminopyridinium iodides were obtained by alkylation of corresponding Py derivatives by bromoethane or iodomethane, respectively; purity of precursors was confirmed by element analysis and ^{1}H NMR. Elemental analysis (EA) was performed on a Euro NA 3000 Elemental Analyzer (EuroVector). **12** was prepared according to the previously published procedure [17]; **13** was obtained by the same scheme as **1**–**11** (see below).

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